Casimir effects in atomic, molecular, and optical physics

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Abstract

The long-range interaction between two atoms and the long-range interaction between an ion and an electron are compared at small and large intersystem separations. The vacuum dressed atom formalism is applied and found to provide a framework for interpretation of the similarities between the two cases. The van der Waals forces or Casimir-Polder potentials are used to obtain insight into relativistic and higher multipolar terms.

Key words: Casimir effect, van der Waals potential, Casimir-Polder potential
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Contents

1 Introduction

Distance changes everything. The same is the case for electromagnetic interaction potential energies between polarizable systems. In atomic, molecular, and optical physics the small retarded van der Waals (or Casimir-Polder) potentials between pairs of polarizable systems (either of which is an atom, molecule, surface, electron, or ion) for separations at long-ranges where exchange forces are negligible have been well-studied theoretically. There are also three- and higher-body potentials, cf. (Salam, 2010), antimatter applications (Voronin et al., 2005), and more. Much of the current interest in the Casimir interactions between atoms and walls is due to interests related to nanotechnologies, cf. (Capasso et al., 2007), and related attempts to engineer repulsive forces at nano-scales (Marcus, 2009). Numerous topical surveys and reviews, monographs, book chapters, conference proceedings, and popular texts touching on particular pairwise potentials are in print—literally a "mountain of available information" (Bonin and Kresin, 1997, p.185)—and many sources contain extensive bibliographies. It is not uncommon to run across statements indicating that there has been a rapid increase in the number of available papers related to the Casimir effect. Even a recent book, *Advances in the Casimir effect* (Bordag et al., 2009), focusing mainly on recent results, comes to over 700 pages.

This paper is concerned with bringing to light some connections between theoretical results from various formulations for the zero temperature limits of interactions between ground state atoms, ions, or molecules. The case has been advanced that the practical relevance of zero temperature results is questionable, see Wennerstrom et al. (1999), and although the case is reasonable, you have to start somewhere. The present article is therefore more selective than comprehensive and it is organized as follows. In Sec. 2 the microscopic and macroscopic natures of Casimir effects are very briefly surveyed and the interaction between two atoms is reviewed in Sec. 3 including discussion of the terms of relativistic origin arising for small atomic separations. In Sec. 4 the change in the form of the interaction, when one of the two polarizable systems is charged, is studied. The vacuum dressed atom approach is introduced and applied to the case of an electron and an ion in Sec. 5 and it is used in Sec. 6 to gain insight into the origin of the numerical factor "23" in expressions for potentials related to the Casimir effect. Finally in Sec. 7 the treatment of multipoles beyond the electric dipole is discussed for two atoms and for an electron and an ion.

2 What's a micro effect; what's a macro effect?

The picture of two well-spaced systems interacting through fluctuating electromagnetic fields can describe many phenomena. The usual definitions are that the *Casimir-Polder* potential (Casimir and Polder, 1948) is the retarded interaction between two atoms or an atom and a wall and a *Casimir effect* (Casimir, 1948) is the "observable non-classical electromagnetic force of attraction between two parallel conducting plates" (Schwinger, 1975). Milton (2001, p.3) traced the change in Casimir's perspective from action at a distance (Casimir and Polder, 1948) to the local action of fields (Casimir, 1948) or an equivalence in physical pictures of fluctuating electric dipoles or fluctuating electric fields. The conceptual realizations of the Casimir effect and of the Casimir-Polder potential have been extended well beyond their original theoretical models; an extensive tabulation can be found in (Buhmann and Welsch, 2007). The term Casimir effect will be used rather more loosely in the present work recognizing in advance the connection already established in the literature with the more general pictures of "dispersion forces" (Mahanty and Ninham, 1976) or "van der Waals forces" (Barash and Ginzburg, 1984; Parsegian, 2006). Also as noted by Barton (1999) "By tradition, 'Casimir effects' denote *macroscopic* forces and energy shifts; yet for connected bodies the macroscopic must be matched to *microscopic* physics, and no purely macroscopic model can be guaranteed in advance to reproduce the results of this matching adequately for whatever purpose is in hand." And as Barash and Ginzburg (1984) write, "The fluctuation nature of van der Waals forces for macroscopic objects is largely the same as for individual atoms and molecules. The macroscopic and microscopic aspects of the theory of van der Waals forces are therefore intimately related." Moreover, there are macroscopic formulations that can yield results for microscopic systems by taking various limits (Milonni and Lerner, 1992; Spagnolo et al., 2007; Buhmann and Welsch, 2007), but local field corrections require close study (Henkel et al., 2008).

For the present purposes, the concern is largely with pair-wise potentials and their comparison with results from various approaches. Atomic units with $\hbar = e = m_e = 1$ are used throughout, wherein the fine structure constant is $\alpha = 1/c$, though for some formulae $\hbar$ and c are restored. It is useful to define the reduced Compton wavelength of the electron $\lambda\!\!\!^{-}_{\rm C} \equiv \hbar/m_e c$. The notational convention of Spruch and Tikochinsky (1993) is followed where the subscripts At, Ion, and El denote, respectively, an atom, ion, and electron.

The Casimir-Polder potential for the interaction between two identical atoms is written as (Casimir and Polder, 1948)

$$V_{\rm AtAt}(r) = -\frac{1}{\pi r^6}\int_0^\infty d\omega\ \exp(-2\alpha\omega r)[\alpha_e(i\omega)]^2 P(\alpha\omega R), \tag{1}$$

with

$$P(x) = x^4 + 2x^3 + 5x^2 + 6x + 3, \tag{2}$$

and where the dynamic (frequency dependent) electric dipole polarizability is

$$\alpha_e(\omega) = \sum_u \frac{f_u}{E_{u0}^2 - \omega^2}, \tag{3}$$

f_u is the electric dipole oscillator strength from the ground state 0 to the excited state u, $E_{u0} = E_u - E_0$ is the energy difference, the summation includes an integration over continuum states, and ω is the frequency. An alternative form of Eq. (1) (Boyer, 1969; Spruch and Kelsey, 1978) is

$$V_{\rm AtAt}(r) = -\frac{\hbar c}{\pi} \lim_{\mu \to 0} \int_0^\infty dk\ k^6 e^{-\mu k} [\alpha_e(\omega)]^2 I(kr), \tag{4}$$

with $\omega = kc$ and where

$$I(x) = \sin(2x)(x^{-2} - 5x^{-4} + 3x^{-6}) + \cos(2x)(2x^{-3} - 6x^{-5}). \tag{5}$$

The interaction potentials given in Eqs. (1) and (4) are valid for all separations larger than some tens of a_0, and do not take into account electron charge cloud overlap, spin, magnetic susceptibilities, for example, though these have all been studied. The interaction potential $V_{\rm AtAt}(r)$, given by either Eq. (1) or (4), does contain the van der Waals interaction, certain relativistic effects, and higher order effects, as well as the asymptotic form first obtained by Casimir and Polder (1948),

$$V_{\rm AtAt}(r) \to -23 \frac{\hbar c}{4\pi r^7} [\alpha_e(0)]^2, \qquad r \to \infty. \tag{6}$$

For the hydrogen atom, $\alpha_e(0) = \frac{9}{2}$.

3 Relativistic terms

Before studying the long-range Casimir-Polder interaction potential in detail, it is useful to look at the "small r" expansion [1] of the full potential Eq. (1) for distances, say, of the order 20 a_0.

[1] The term "short-range" is avoided and reserved for exchange, overlap, and forces that are, for example, exponentially decaying (Barash and Ginzburg, 1984). Thus,

Expanding Eq. (1) for small r, the potential is

$$V_{\mathrm{AtAt}}(r) \sim -\frac{C_6}{r^6} + \alpha^2 \frac{W_4}{r^4} + \mathcal{O}(\alpha^3/r^3), \qquad r \sim 20\ a_0. \tag{7}$$

The first term in the expansion is the van der Waals potential with van der Waals constant,

$$C_6 = \frac{3}{\pi} \int_0^\infty d\omega\ [\alpha_e(i\omega)]^2, \tag{8}$$

and for two H atoms, $C_6 = 6.499\,026\,705\,405\,84$ (Watson, 1991).

The term of order α^2 relative to the van der Waals potential is a relativistic correction

$$W_4 = \frac{1}{\pi} \int_0^\infty d\omega\ \omega^2 [\alpha_e(i\omega)]^2, \tag{9}$$

which can be traced back (Power and Zienau, 1957) to the "orbit-orbit" effective potential appearing in the Breit-Pauli reduction of the Dirac equation (Meath and Hirschfelder, 1966).

The numerical value of W_4 for two H atoms is $0.462\,806\,538\,843\,273$ according to Watson (1991), who used a momentum space approach and expansion in Pollaczek polynomials; he also obtained the highly accurate value of C_6 quoted above. Certain exact representations of the dynamic polarizability function of H also facilitate evaluations of W_4 (Deal and Young, 1971) and of C_6 (O'Carroll and Sucher, 1968).

Small relativistic terms were applied in a few cases to potential energy functions of light diatomic molecules, see for example Przybtek et al. (2010), and where improved accuracies were sought for precision calculations, for example, such as those of low-energy ultra-cold atomic collisions (Zygelman et al., 2003) or of the ionization potential of the hydrogen molecule (Piszczatowski et al., 2009).

Recently Pachucki (2005) reanalyzed the Casimir-Polder potential complete to terms of $\mathcal{O}(\alpha^2)$, but expressed it in such a way that its form is valid over

the term "long-range" interaction potential here will indicate the form valid for intersystem separations, typically from several to tens of a_0 to infinity, such as those in Eq. (1) and (4), which have a "small r" expansion, Eq. (7) and a "large r" expansion Eq.(6)

all distances sufficiently large that the atomic wave functions don't overlap; not just in the large r limit.

4 Yet another repulsive interaction

In the previous section, the original Casimir-Polder potential was introduced and seen to be attractive, but there are several known cases where repulsive potentials have been predicted theoretically. [2] Thus, Feinberg and Sucher (1968, 1970) used a general dispersion-theoretic scattering approach to show that the potential given in Eq. (6) can be generalized for two systems A and B to an expression bilinear in the electric and the magnetic polarizabilities of each system,

$$V_{\rm AtAt}(r) \sim -\frac{\hbar c}{4\pi r^7}[23(\alpha_e^A\alpha_e^B + \alpha_m^A\alpha_m^B) \\ -7(\alpha_e^A\alpha_m^B + \alpha_e^B\alpha_m^A)] + \mathcal{O}(r^{-9}), \qquad r \sim \infty \tag{10}$$

where α_e^A and α_e^B are the static polarizabilities $\alpha_e(0)$, respectively, of A and B, and α_m^A and α_m^B, with $\alpha_m \equiv \alpha_m(0)$, are, respectively, the static magnetic polarizabilities of A and B. Note that the cross term in the potential containing the product of α_e and α_m leads to a repulsive force. [3] More detailed discussions concerning the treatment of the magnetic terms for the interaction between two atoms can be found in Salam (2000, 2010).

There is another repulsive Casimir-Polder potential, perhaps not as well known. For the scattering interaction between a charged, structureless particle B and a neutral polarizable particle A (Bernabéu and Tarrach, 1976; Spruch and Kelsey, 1978) or for the interaction between a charged, structureless particle B and an ion A (Kelsey and Spruch, 1978b; Spruch and Kelsey, 1978), there is an interaction (for B an electron) given by

$$V_{\rm AtEl}(r) \sim V_{\rm IonEl}(r) \sim \frac{\lambda\!\!\!^{-}_{\rm C} e^2}{4\pi r^5}[11\alpha_e^A + 5\alpha_m^A], \qquad r \sim \infty. \tag{11}$$

For either of the the two cases (the target is neutral or it is charged) the asymptotic result Eq. (11) applies, but the complete potentials including other

[2] V. Hushwater, *Survey of Repulsive Casimir Forces,* unpublished talk, ITAMP Casimir workshop, Cambridge, MA, November 16, 2002.

[3] The $\alpha_e^A\alpha_m^B$ term supports the result that the interaction between two plates is repulsive, if one plate (A) has only infinite permittivity and one plate (B) is only infinitely permeable (Boyer, 1974); an alternative argument not making use of Eq. (10) is given by (Schaden and Spruch, 1998).

corrections are not identical, due to the remnant $1/r$ Coulomb interaction in the charged particle and ion case higher order corrections at large r differ, as emphasized by (Au, 1986, 1989).

The long-range Casimir potential $V_{\rm IonEl}(r)$ is the present object of interest but it is useful sometimes to write the full potential with "instantaneous" Coulomb interactions as well. Therefore, the full potential $U(r)$, including the charged particle and ion electric interactions (but neglecting the dominant $1/r$ Coulomb potential), is at large r

$$U(r) = -\frac{1}{2}e^2\alpha_e r^{-4} + \frac{11}{4\pi}\lambda\!\!\!^{-}_{\rm C}e^2\alpha_e r^{-5}... \qquad r \sim \infty, \tag{12}$$

where α_e is the polarizability of the ion. The first term in Eq. (12) is the polarization potential. The second term is the asymptotic Casimir-Polder-type interaction, which was confirmed theoretically (Feinberg and Sucher, 1983; Au, 1986). The Casimir-Polder potential for the interaction between an electron and an ion was expressed in a fashion similar to the result for two atoms given in Eq. (1) by Au et al. (1984) using a dispersion-relation analysis, and later using Coulomb gauge, old-fashioned perturbation theory by Babb and Spruch (1987) and Au (1988).

It can be expressed (Babb and Spruch, 1987) in the compact form similar to Eq. (4),

$$V_{\rm IonEl}(r) = \frac{e^2}{\pi}\lambda\!\!\!^{-}_{\rm C}\lim_{\mu\to 0}\int_0^\infty dk\; e^{-\mu k}k^4F(k)I(kr), \tag{13}$$

where

$$F(k) = \sum_u f_u/[E_{u0}(E_{u0}+E_k)]. \tag{14}$$

Taking account of the Coulomb interactions, the potential has the expansion for small r,

$$U(r) + V_{\rm IonEl}(r) \sim -\frac{1}{2}e^2\alpha_e r^{-4} + 3\beta r^{-6} + (\alpha^2/Z^2)r^{-4}..., \quad r \sim \text{a few } a_0, \tag{15}$$

where Z is the charge of the ion, and $\beta = \frac{43}{8}Z^{-6}$ (Kleinman et al., 1968; Dalgarno et al., 1968). Note the disappearance for small r of the r^{-5} term that was present in the large r potential, Eq. (12).

It was emphasized by Kelsey and Spruch (1978a) and Feinberg et al. (1989)

that that the $3\beta r^{-6}$ term disappears at large r. Thus, the potential can be written in the form (Babb and Spruch, 1987)

$$V_{\rm IonEl}(r) + 3\beta r^{-6} = -\frac{\hbar c}{\pi} \lim_{\mu\to 0} \int_0^\infty dk\ k^6 e^{-\mu k} I(kr) \times\{\alpha_e(k)\alpha_{\rm out}(k) - 2\frac{\hbar c}{e^2}\alpha_{\rm out}(k)[\beta(k) - \beta]\}, \tag{16}$$

using

$$\alpha_{\rm out}(\omega) = -e^2/m\omega^2, \tag{17}$$

$$F(k) = \alpha_e(k) - 2\frac{k}{\alpha}\beta(k), \tag{18}$$

and

$$\beta(k) = \frac{1}{2}\sum_u f_u/[E_{u0}(E_{u0}^2 + E_k^2)]. \tag{19}$$

The effective potential Eq. (13) was evaluated numerically and used to study theoretically the energy shift arising from the interaction between an electron bound in a high Rydberg state $|ln\rangle$ with principal quantum number n, and with angular momentum $l \sim n$. Experiments on highly excited $n = 10$ Rydberg states of He were carried out ands several theoretical formulations were developed. The details about experiments and theories, and their comparisons, are very completely presented in the book edited by Levin and Micha (1992), see also (Hessels, 1992; Stevens and Lundeen, 2000; Drake, 1993; Lundeen, 2005). Many other terms must be considered carefully in the theoretical calculations; the details don't directly relate further though to the present paper.

Recently two groups have reproduced the electric (α_e) part of Eq. (11) using different arguments, but both approaching the interaction between a charged particle and a neutral particle as one loop quantum field theoretic calculations. Panella et al. (1990) obtained Eq. (11) and and traced the r^{-5} result result back to a change in the mass induced by "condensed-matter renormalization" of the electromagnetic fluctuations (Panella and Widom, 1994). The repulsive potential is attributed to soft-photon infrared renormalization. In contrast, Holstein and Donoghue (2004) were seeking to identify cases where classical effects are found within one-loop diagrams. Using an effective field theory approach, they find quantum corrections to the classical polarization potential; their result is identical to the α_e part of Eq. (11). They identify the r^{-5} term as a quantum correction to the polarization potential, which arises from the infrared behavior of the Feynman diagrams, when at least two massless propagators occur in a loop contribution.

In a subsequent study, Holstein (2008) obtained Eq. (11) and observed that the r^{-5} term in Eq. (11) might be associated with zitterbewegung and he noted that, under the influence of this effect, "in the quantum mechanical case the distance between two objects is uncertain by an amount of order the Compton wavelength due to zero point motion," $\delta r \sim \lambda\!\!\!^{-}_{\rm C}$, hence

$$V(r) \sim \frac{1}{r^4} \to \frac{1}{(r \pm \delta r)^4} \approx \frac{1}{r^4} \mp 4\lambda\!\!\!^{-}_{\rm C} \frac{1}{r^5}. \tag{20}$$

It is an intriguing argument, though the ambiguity of the sign is unresolved. Zitterbewegung would normally be attributed to virtual electron-positron transitions (Milonni, 1994, p. 322) at the length scale less than $\lambda\!\!\!^{-}_{\rm C}$, which would seemingly place the effect outside of the realm of the low energy fluctuation arguments used by, for example, Spruch and Kelsey (1978) in deriving Eq. (11). Nevertheless, the calculations of Holstein and Donoghue (2004) are concerned with large r, so there must be a connection to the scale of $\lambda\!\!\!^{-}_{\rm C}$ and this will be addressed in the next section.

The effective field theory of Holstein (2008) allows the longest-range parts of electromagnetic scattering processes to be isolated, and he extended the asymptotic (large r) results for the interactions between two systems, with and without spin, to the case where one or both systems are electrically neutral; see also Sucher and Feinberg (1992).

5 Nonrelativistic molecules and dressed atoms

In the theoretical "vacuum dressed atom" approach, a ground state "bare" atom interacts with the vacuum electromagnetic field. The combination system of the atom and the field is taken to be in the lowest possible energy state of the noninteracting atom-field system, and the zero-point fluctuations of the field are seen as inducing virtual absorption and re-emission of photons in the atom—the "vacuum dressed atom" is then the system comprised of the atom and the associated cloud of virtual photons (Compagno et al., 1995a,b). A good account of the development of the concept of atoms dressed by the vacuum electromagnetic field is given by Compagno et al. (2006). The energy density can be calculated and used to obtain expressions for long-range potentials and other physical quantities, as was shown in quantum optics (Compagno et al., 1995b; Cirone and Passante, 1996; Salam, 2010) for the nonrelativistic free electron interacting with the vacuum electromagnetic field and the nonrelativistic hydrogen atom.

Compagno and Salamone (1991) [see also Compagno et al. (1995b)] considered a slow electron interacting with the vacuum field. The key observation is

that the cloud around the electron is due to emission and reabsorption of virtual photons in the course of recoil events. They point out the zitterbewegung due to relativistic fluctuations would enter and contribute a cloud of size of order $\lambda\!\!\!^{-}_{\rm C}$. This effectively limits their nonrelativistic model to distances $\gg \lambda\!\!\!^{-}_{\rm C}$, so that the positron cloud can be neglected and the electron has the physical charge $-e$, accordingly, only low frequency photons enter. In this picture the virtual cloud affects the field surrounding the charge and changes the average values of the squares of the electric and magnetic fields.

They calculate the classical and quantum contributions to the energy density around the electron both moving and at rest and for the electron at rest, they find (for $r \gg \lambda\!\!\!^{-}_{\rm C}$)

$$\langle E_{\rm e}(r)\rangle = \frac{e^2}{8\pi r^4} + \frac{5}{16\pi^2}\frac{e^2}{r^4}\frac{\lambda\!\!\!^{-}_{\rm C}}{r} + \frac{\hbar c}{4V}\sum_k k \tag{21}$$

and

$$\langle E_{\rm m}(r)\rangle = -\frac{5}{16\pi^2}\frac{e^2}{r^4}\frac{\lambda\!\!\!^{-}_{\rm C}}{r} + \frac{\hbar c}{4V}\sum_k k, \tag{22}$$

where $E_{\rm e}(r)$ and $E_{\rm m}(r)$ are, respectively, the electric and magnetic energy densities at a distance r from the electron, V is the quantization volume, and the sum is over the vacuum field modes.

For the present purpose, one of their key observations is the appearance of the r^{-5} contribution which Compagno and Salamone (1991) attribute to the virtual photon cloud surrounding the electron fluctuations that arise due to interference between the virtual photons emitted and absorbed by the electron and zero-point field fluctuations. The r^{-5} term is deemed purely quantum in nature (Compagno et al., 1995b). The energy densities can be directly related to the Casimir-Polder potential, as noted by Passante and Power (1987). What is striking is the similarity in form between Eqs. (21) and (22) and the large r potential for the interaction of an electron and an ion, Eq. (12). Evidently, both the classical polarization potential and the retarded asymptotic Casimir-Polder potential are present.

As discussed above, Holstein and Donoghue (2004) showed that, within a diagrammatic, effective field theory approach, classical effects can arise. In particular, the energy density of a particle in a plane wave calculated by Holstein and Donoghue (2004) agrees in form with the dressed electron result containing both a r^{-4} polarization potential and the "purely quantum" r^{-5} asymptotic retarded potential.

For the nonrelativistic hydrogen atom, the analysis was carried out again

within the vacuum dressed atom formalism; the extensive calculations can be found in (Passante and Power, 1987; Compagno et al., 1995b; Compagno et al., 2006). The analysis is complicated, but it is similar to that carried out by Babb and Spruch (1987) and Au (1989). For example, Eq. (7.148) of Compagno et al. (1995b) describes the longitudinal electric field and transverse electric field contributions to the energy density around a hydrogen atom,

$$\frac{1}{4\pi}{}'\langle\phi|E_{||}(\mathbf{x}) - E_{\perp}(\mathbf{x})|\phi\rangle' \sim \frac{1}{r^3}\int \frac{k^2 j_2(kr)}{\omega_N + \omega_k} dk \tag{23}$$

and it is almost identical to V_{IT}, Eq. (4.16) found by Babb and Spruch (1987) for the contribution of one instantaneous Coulomb photon and one transverse photon to the effective potential in the case of an electron and an ion.

In an earlier study using the virtual photon cloud picture, Passante and Power (1987) note that the r^{-6} term in the description of the energy density around a ground state hydrogen atom disappears at large r similarly to the way the van der Waals form r^{-6} form is replaced at asymptotic distances by the r^{-7} form. They find that nonretarded effects of order $\sim r^{-6}$ in the energy density are absent in the far zone of the hydrogen atom and they obtain the simple form for the energy density with an $\mathcal{O}(r^{-7})$ term related to the virtual charge cloud,

$$\frac{1}{8\pi}\langle\Psi|F^2|\Psi\rangle - E_{zp} = \frac{23}{16\pi^2}\frac{\hbar c}{r^7}\alpha_e, \tag{24}$$

where F is the electric field.

Radożycki (1990) carried out a relativistic calculation of the electromagnetic virtual cloud of the ground state hydrogen atom using a Dirac formalism. According to Compagno et al. (2006) his work was supposed to be an independent calculation of the energy density of the vacuum dressed hydrogen atom. For the energy density due to the electric field, his result in the large r limit is

$$\begin{aligned}\frac{1}{2}\langle F^2(\mathbf{r})\rangle = \frac{13\hbar c e^2}{16\pi^2}\sum_n \frac{1}{E_{n1}}\langle 1|x|n\rangle\langle n|x|1\rangle\frac{1}{r^7} \\ + \frac{7\hbar c e^2}{16\pi^2}\sum_n \frac{1}{E_{n1}}\langle 1|x_i|n\rangle\langle n|x_j|1\rangle\frac{\hat{r}_i\hat{r}_j}{r^7}.\end{aligned} \tag{25}$$

Identifying the tensor electric dipole polarizability in Eq. (25)

$$2\sum_n \frac{1}{E_{n1}}\langle 1|x_i|n\rangle\langle n|x_j|1\rangle = \alpha_{e,ij}, \tag{26}$$

Eq. (25) agrees with the two-level "Craig-Power" model (Compagno et al., 1995b) result for the energy density in the large r limit,

$$\langle E_e(\mathbf{r})\rangle = \frac{1}{32\pi^2}\hbar c\alpha_{ij}(13\delta_{ij} + 7\hat{r}_i\hat{r}_j)\frac{1}{r^7}. \tag{27}$$

In an unrelated study of the Casimir-Polder potential for an electron interacting with a hydrogen molecular ion core, Babb and Spruch (1994) obtained an expression almost identical to Eqs. (25) and (27). The tensor polarizability arises from the anisotropic interaction arising from the cylindrical symmetry of the diatomic molecule core.

Compagno et al. (1995b) interpret the large r Casimir-Polder potential as the interaction between the vacuum dressed "source" atom with polarizability α_S and the "test" atom with polarizability α_T

$$V(r) = \frac{-23}{4\pi}\hbar c\alpha_S\alpha_T\frac{1}{r^7} = -4\pi\alpha_T\langle E_e^S(\mathbf{r})\rangle, \tag{28}$$

where the energy density is generated by the source at point $\mathbf{r}$ in the absence of the test atom.

Another interesting point emphasized by Compagno et al. (1995b) is that

$$V(\mathbf{r}) = -4\pi\alpha_T\langle E_e^S(\mathbf{r})\rangle, \tag{29}$$

"thus the van der Waals force provides a means of measuring directly the electric energy density of a source both in the near and in the far regions."

6 Not a trivial number

In his contribution to the proceedings of a conference held in Maratea, Italy, [4] Casimir (1987) wrote,"In the theory of the so-called Casimir effect two lines of approach are coming together. The first one is concerned with Van der Waals forces, the second one with zero-point energy." Today, that connection is well-established, though the "reality" of zero-point energy is still debatable; see the very accessible article by Rugh et al. (1999), and also Jaffe (2005).

In Eq. (6), it was shown that the asymptotic potential for the interaction between two electrically polarizable particles contains the factor 23, as does the asymptotic potential for two magnetically polarizable particles, see Eq. (10).

[4] June 1–14, 1986

The factor 23 has reappeared in other situations. In the asymptotic interaction between and electron and an ion, expanding Eq. (16) for large r and keeping one more term past that given in Eq. (12), (Feinberg and Sucher, 1983), the potential is

$$\begin{aligned} U(r) &\sim -\frac{1}{2}e^2\alpha_e r^{-4} + V_{\rm IonEl}(r) \\ &\sim -\frac{1}{2}e^2\alpha_e r^{-4} + \frac{11}{4\pi}\lambda\!\!\!^{-}_{\rm C} e^2 \frac{\alpha_e}{r^5} + \frac{23}{4\pi}\frac{e^2\lambda\!\!\!^{-}_{\rm C}}{a_0^2}\frac{\gamma(0)}{r^7} + ..., \quad r \sim \infty. \end{aligned} \tag{30}$$

According to Feinberg et al. (1989), when told of this result [that is, Eq. (30)], at the Maratea conference, Casimir replied, "23 is not a trivial number. I am happy to see that." However, the appearance of the 23 in a way nearly identical to the result for the asymptotic atom-atom potential was not explained completely (Feinberg and Sucher, 1983). In addition, the sign of the term containing 23 is opposite to that for the case of two atoms.

Evidently, while the complete potential for the electron-ion case can be expressed as Eq. (13), expansion for large r yields the two terms of Eq. (11). I conjecture that the $\mathcal{O}(r^{-5})$ term can be interpreted as the effective potential arising from the energy density of the weakly bound, vacuum dressed, electron "source" interacting with the ion core "test" α_e,

$$\alpha_e\langle E^2_{\rm out}\rangle \sim \alpha_e(\frac{1}{r^4} + \lambda\!\!\!^{-}_{\rm C}\frac{1}{r^5}), \tag{31}$$

in accord with the ideas of Compagno and Salamone (1991), supported by the large r one loop calculations of Holstein and Donoghue (2004) and Holstein (2008). The other term $\sim r^{-7}$ can be interpreted as the source term of the fluctuating vacuum dressed polarizable ion core "source" acting on the electron "test" particle,

$$-4\pi\alpha_{\rm out}(\bar\omega)\langle\bar E^S_e(\mathbf{r})\rangle \sim -\alpha_{\rm out}(\bar\omega)\frac{23}{4\pi}\hbar c\gamma r^{-7}, \tag{32}$$

where $\bar E^S_e$ indicates that the electric field energy density is modified due to the Coulomb binding and $\bar\omega$ is a characteristic energy. This is to be expected based on arguments given by (Au, 1986, 1989) for the Rydberg helium case and by Compagno and Salamone (1991) for the vacuum dressed slow electron and vacuum dressed hydrogen atom. Using Eq. (17) for $\alpha_{\rm out}(k) = -\lambda\!\!\!^{-}_{\rm C}\alpha k^{-2}$, where $kc = \omega$, evaluated at $\bar\omega = \alpha c/a_0$ (Feinberg and Sucher, 1983) Eq. (32) yields a term in general agreement with Eq. (30),

$$-4\pi\alpha_{\rm out}(\bar\omega)\langle\bar E^S_e(\mathbf{r})\rangle \sim +\lambda\!\!\!^{-}_{\rm C}\frac{23}{4\pi}\gamma r^{-7}. \tag{33}$$

The approach of adding the two interactions is consistent with the interpretation of the fluctuating field approach to Casimir-Polder interactions proposed by Power and Thirunamachandran (1993). Namely, that the dipole in each particle is induced by the vacuum fluctuations of the electromagnetic field.

7 Reconciling multipoles

7.1 Two atoms

The extension beyond electric and magnetic dipoles for the retarded van der Waals (or Casimir-Polder) potential between two neutral spinless systems was achieved by Au and Feinberg (1972). Using scattering analysis they were able to obtain integral forms for the complete potential for each multipole, valid for all separations greater than some tens of a_0, and they gave the first several terms in each of the small r and large r expansions of the potentials. Their result, as noted by Feinberg (1974), and as emphasized by Power and Thirunamachandran (1996), included the property "that the expansions of the electric (magnetic) form factors include high-order magnetic (electric) susceptibilities in addition to electric (magnetic) polarizabilities."

The first several electric multipole results of Au and Feinberg (1972) were used for applications to calculations of the binding energy of the helium dimer by Luo et al. (1993) and by Chen and Chung (1996) and for applications to ultracold atom scattering by Marinescu et al. (1994), who evaluated the expressions for a pair of hydrogen atoms and for a pair of like alkali-metal atoms.

A few years later, in a thorough analysis, Salam and Thirunamachandran (1996) and Power and Thirunamachandran (1996) pointed out that the results of the Au and Feinberg (1972) analysis did not concur with other results obtained evidently independently by Jenkins et al. (1994) who used a different approach. Power and Thirunamachandran (1996) argued that the correct form for the next order Casimir-Polder interaction, arising from the interaction of an electric dipole and an electric quadrupole is

$$V_{12}(r) = -\frac{1}{3\pi}\int_0^\infty d\omega \exp(-2\alpha\omega r)\alpha_e(i\omega)\alpha_{e;2}(i\omega)P_{12}(\omega\alpha r), \tag{34}$$

where $\alpha_{e;2}$ is the electric quadrupole polarizability and

$$P_{12}(x) = \tfrac{1}{2}x^6 + 3x^5 + \tfrac{27}{2}x^4 + 42x^3 + 81x^2 + 90x + 45. \tag{35}$$

For small r,

$$V_{12}(r) \sim -\frac{C_8}{r^8} + \alpha^2 \frac{W_6}{r^6} + ..., \tag{36}$$

where

$$C_8 = \frac{15}{\pi} \int_0^\infty d\omega \; \omega^2 \alpha_e(i\omega) \alpha_{e;2}(i\omega), \tag{37}$$

and the coefficient of the relativistic correction is

$$W_6 = \frac{3}{\pi} \int_0^\infty d\omega \; \omega^2 \alpha_e(i\omega) \alpha_{e;2}(i\omega) \tag{38}$$

Meath and Hirschfelder (1966) obtained the relativistic corrections of relative order α^2 for two hydrogen atoms. For the orbit-orbit interaction $H_{LL;0}$, the corresponding effective potential contributions arise as powers of r^{-4} and r^{-6}. Their approach is not valid in the large r limit, but it should agree with the small r form of $V_{\mathrm{AtAt}}(r)$ and $V_{12}(r)$.

In turn Marinescu et al. (1994) noticed a discrepancy between the result of Meath and Hirschfelder and Johnson et al. (1967) for the r^{-6} relativistic term for small distances and the result obtained by expanding the potential of Au and Feinberg for small r. In contrast, expansion of the revised dipole-quadrupole potential $V_{12}(r)$ of Jenkins et al. (1994) for small r provides a value for W_6, see Eq. (38), in agreement with the expression of Meath and Hirschfelder (1966) and Johnson et al. (1967) for the r^{-6} term in the expansion of the Breit-Pauli equation. Accordingly, earlier results, such as the results of (Chen and Chung, 1996) for W_6 in should be multiplied by $\frac{3}{2}$.

Later, Marinescu and You (1999) rederived the atom-atom potential accounting for magnetic and other terms to higher order, see also (Salam, 2000). Marinescu and You note that numerically, at least, for their evaluations of the like alkali-metal atom pairs, that the relative error between results from the two approaches is smaller than 10^{-5}. In any case, other terms, such as mass polarization, Darwin interaction terms, and Lamb shifts, would have to be included at the correct order for a complete description.

Asymptotically, for large r (Thirunamachandran, 1988; Jenkins et al., 1994; Yan et al., 1997; Marinescu and You, 1999)

$$V_{12}(r) \sim -\frac{531\hbar c}{16\pi r^9} \alpha_e(0) \alpha_{e;2}(0). \tag{39}$$

Feinberg (1974) expected that for atoms—with the exception of possibly the magnetic-magnetic case for two hydrogen atoms, see (Feinberg and Sucher, 1968)—magnetic and higher order multipole effects would be negligible for domains where retardation was important. Thus, Feinberg was motivated to use the scattering approach to study the case of two superconducting spheres and he obtained a series in powers of the sphere-sphere separation distance.

Using a new formalism based on a scattering approach, Emig (2008); Emig and Jaffe (2008) investigated the Casimir energy between two spheres. For large separations, they obtain an expansion in the separation distance r. The lead term is of order r^{-7} and is given by Eq. (10), where the polarizabilities correspond to those of the spheres. Moreover, the next term, of order r^{-9} is given by Eq. (39). In another calculation using the scattering approach, Emig (2010) obtains the large r interaction potential for two anisotropic objects; his result is in agreement with the earlier results for two anisotropic particles given by Craig and Power (1969).

7.2 An electron and an ion

Expanding Eq. (13) for small r, it was shown above in Eq. (15) that there is a term $(\alpha^2/Z^2)r^{-4}$. This relativistic term is identical to the atom-atom case, which is known to result from perturbation treatment of the Breit interaction with the Coulomb interaction (Power and Zienau, 1957; Au, 1989).

Some time after Eq. (4) was obtained, the complete long-range potential including multipoles for an ion and a neutral spinless system was obtained by Feinberg and Sucher (1983) and by Au (1985). According to Hessels (1992), the result of Au (1985) for the next term is

$$V_{E,1}(r) = \tfrac{9}{16}\alpha^2 r^{-6}. \tag{40}$$

Hessels (1992) carried out a perturbation theoretic calculation of the relativistic corrections for the ion-electron system, analogously to the calculation of Meath and Hirschfelder (1966) for the atom-atom interaction. His analysis is in disagreement with Au (1985), but in agreement with comprehensive calculations by Drake (1992), indicating an unresolved discrepancy between the dispersion theoretic result and perturbation theoretic results at $\mathcal{O}(\alpha^2 r^{-6})$ for small r limit of the the ion-electron system.

8 Conclusion

The Casimir effects for the interaction between two atoms and for the interaction between an ion and an electron were investigated and, respectively, their expansions lead to asymptotic terms of order r^{-7} and r^{-5}. The second correction at large r for the ion and electron case is similar to the leading term at large r for the case of two atoms. It was shown that the vacuum dressed atom picture provides a framework for interpretation of this similarity.

Reconciliation of interaction potentials for electric dipole and electric quadrupole multipoles between atom-atom and ion-electron cases led to insight concerning a discrepancy between a scattering dispersion theoretic calculation and a perturbation theoretic calculation of the ion-electron interaction for the electric quadrupole relativistic term.

As interest in the potential applications of Casimir effects in atomic, molecular, and optical physics increases, limiting results for interaction potentials at zero temperature—such as those presented here—may provide useful insights and checks on calculations for more complicated geometries. Hopefully, it will be a long time until it is true that *nothing can be added to vacuum studies.*

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